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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 16020-WO-03	FOR FURTHER ACTION		See Form PCT/PEA/416
International application No. PCT/IL2004/000615	International filing date (day/month/year) 08.07.2004	Priority date (day/month/year) 10.07.2003	
International Patent Classification (IPC) or national classification and IPC C08L23/00, C08J3/24, C08F255/02			
Applicant CARMEL OLEFINS LTD. et al.			
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau a total of 4 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input checked="" type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>			
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input checked="" type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>			
Date of submission of the demand 08.05.2005		Date of completion of this report 31.10.2005	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized Officer Iraegui Retolaza, E Telephone No. +49 89 2399-8490	



**INTERNATIONAL PRELIMINARY REPORT
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International application No.
PCT/IL2004/000615

Box No. 1 Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4)
 - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1-24 as originally filed

Claims, Numbers

8-21, 22(part) as originally filed

1-7, 22(part), 23-33 received on 08.05.2005 with letter of 08.05.2005

- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing *(specify)*:
 - ☐ any table(s) related to sequence listing *(specify)*:
4. ☒ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
 - ☒ the claims, Nos. 4
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing *(specify)*:
 - ☐ any table(s) related to sequence listing *(specify)*:

* If item 4 applies, some or all of these sheets may be marked "superseded."

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Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-33
	No: Claims	
Inventive step (IS)	Yes: Claims	1-33
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-33
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

D1: DE 44 02 943 A (RUSTIGE BERNHARD GMBH & CO KG) 3 August 1995 (1995-08-03)

Document D1 discloses a two phase thermoplastic material consisting of a microdispersion of silane-crosslinked polyethylene (PE) in a continuous, fluid polypropylene (PP) matrix. The silane-grafted PE is dynamically crosslinked by adding a crosslinker during the mixing process, which is carried out in a mixer suitable for the dispersion of the crosslinking structure. A number of crosslinking agents is disclosed as being suitable to carry out the invention according to D1, DBTL (dibutylzinnilaurate having been exemplified (see the passages cited in the International search report together with page 3, lines 27 to 32 of D1).

The subject-matter of claim 1 differs from the disclosure of D1 in that the crosslinking agent is specified to be an acid (Article 33(2) PCT).

The problem to be solved by the present International application is to provide a process for making thermoplastic vulcanizates, wherein full vulcanization of the elastomers used is carried out (see page 4, lines 10 to 12).

The solution proposed involves the use of an acid as crosslinker, which results in thermoplastic vulcanizates exhibiting gel contents of greater than 95%. This solution was not obvious to the man skilled in the art in view of D1 either alone or in combination with the other documents cited in the International search report (Article 33(3) PCT).

Claims 24 and 31 are also novel and inventive.

Re Item VII

Certain defects in the international application

The subject-matter of claim 4 extends beyond the content of the application documents as originally filed, since page 7, lines 27/28 discloses merely organic sulphonic or carboxylic

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(SEPARATE SHEET)**

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acids, and not **any** organic acid as the present claim does (Article 34 PCT).

CLAIMS

1. Process for the production of thermoplastic vulcanizates, which comprises preparing a mixture of polymeric materials, including a matrix and a disperse phase component, and carrying out dynamic vulcanization of the disperse phase component, said dynamic vulcanization comprising the steps of grafting an organic silane on said disperse phase component, whereby to produce grafted disperse phase component chains, and cross-linking said disperse phase component chains in the presence of a cross-linking agent comprising an acid, said grafting and said cross-linking being carried out in the molten state of said disperse phase component.
2. Process according to claim 1, wherein the organic silane is an alkoxy silane.
3. Process according to claim 1, wherein said cross-linking agent is selected from the group consisting of inorganic acid, organic acid, anhydride of inorganic or organic acid, and polyfunctional compound having acid functionality in combination with an amine compound.
4. Process according to claim 3, wherein said cross-linking agent is selected from the group consisting of boric acid and adipic acid with an amine.
5. Process according to claim 4, wherein the amine of the combinations of adipic acid and an amine is triisopropanol amine or triethanol amine.
6. Process according to claim 1, wherein the dynamic vulcanization is carried out in batch mode.
7. Process according to claim 1, wherein the dynamic vulcanization is carried out in continuous mode.

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temperature;

- c) allowing the grafting to take place;
- d) after the grafting, raising the temperature of the mixture to at least the melting point of the matrix, and the cross-linking agent and antioxidant;
- e) allowing the cross-linking to occur, whereby phase inversion occurs;
- f) optionally, devolatilizing the resulting product;
- g) adding any required additional components, while mixing; and
- h) discharging the final product.

23. Process according to claim 7, comprising the steps of:

- a) feeding at least part of the matrix and all other polymeric components to the feed hopper of an extruder;
- b) feeding silane and peroxide to a feeding zone of the extruder, while cooling said zone;
- c) heating the grafting zone of the extruder to such a temperature as to melt the disperse phase component without melting the matrix;
- d) kneading the resulting mixture;
- e) feeding an additional feeder zone of the extruder the additives needed for causing cross-linking, including cross-linking agents and antioxidants;
- f) if necessary, completing the feeding of the matrix;
- g) mixing and kneading the mixture of the fed components, while heating;
- h) removing the volatiles;
- i) optionally adding extender oil and mixing; and
- k) extruding the resulting product.

24. Thermoplastic vulcanizates prepared in a process according to any one of claims 1 to 23, comprising a matrix and a cross-linked disperse phase, which are thermodynamically incompatible, said vulcanizates having the following properties:

- a) low rigidity;

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- b) high flexibility measured by low Shore hardness between 25A and 60D;
- c) disperse phase content of at least 50% by volume;
- d) high gel content of the vulcanized disperse phase component, preferably greater than 95%;
- e) high cross-link density of the vulcanized disperse phase component;
- f) white color;
- g) non-hygroscopicity;
- h) lack of toxic components; and
- i) narrow gaps (ligaments) between cross-linked disperse phase particles, providing near-continuity of said particles within the matrix.

25. Thermoplastic vulcanizates prepared in a process according to any one of claims 1 to 23, comprising a matrix and a cross-linked disperse phase, which are thermodynamically incompatible, said vulcanizates having the following properties:

- a) low or medium rigidity;
- b) disperse phase content of at least 50% by volume;
- c) high gel content of the vulcanized disperse phase component, preferably greater than 95%;
- d) high cross-link density of the vulcanized disperse phase component of more than $5 \cdot 10^{-5} \text{ mol/cm}^3$;
- e) white color;
- f) non-hygroscopicity;
- g) lack of toxic components;
- h) excellent processability by techniques used for processing thermoplastics, comprising extrusion, molding, thermoforming, blow molding, calendering;
- i) very good impact resistance at room temperature and below 0°C ; and
- k) high melt elasticity and melt strength.

26. Thermoplastic vulcanizates according to claims 24 and 25, wherein the matrix consists of semi-crystalline polymers or amorphous polymers.

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27. Thermoplastic vulcanizates according to claims 24 and 25, wherein the semi-crystalline polymers are chosen in the group consisting of thermoplastic polyesters, polyacetals, polyvinylidene fluoride (PVDF), polycarbonate, polystyrene and styrene copolymers, crystalline polyethylene, ethylene copolymers, polypropylene homopolymer, propylene-ethylene random copolymer, heterophasic propylene-ethylene copolymer and polyamides.
28. Thermoplastic vulcanizates according to claims 24 and 25, wherein the content of matrix is 15 to 80 wt% of the total vulcanizate.
29. Thermoplastic vulcanizates according to claim 24 and 25, wherein the cross-linked disperse phase is chosen from the group consisting of polyethylene having density in the range 0.90 – 0.96 g/cm³, ethylene-alpha-olefin copolymers having density in the range 0.85 – 0.95 g/cm³, ethylene copolymers with vinyl acetate or acrylate or other polar monomers; chlorinated polyethylene, styrene block copolymers, natural rubber, polybutadiene, nitrile rubber, butadiene-styrene rubber, chloroprene rubbers, butyl rubber, hydrogenated rubbers, and blends thereof.
30. Thermoplastic vulcanizates according to claims 24 and 25, wherein the content of the disperse phase is 20 to 85 wt% of the total vulcanizate.
31. Products made from the thermoplastic vulcanizates of any one of claims 24 to 30, by known processing techniques, including extrusion, injection molding, thermiforming, blow molding and calendering.
32. Process according to claim 1, wherein said grafting and cross-linking do not require the addition of water into said mixture of polymeric materials.
33. Process according to claim 1, wherein said disperse phase component comprises more than 95% gel content.

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